

# Compact De-NOxer for Automotive Exhaust

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Britton Chang and Manuel Garcia

Our two year project concluded with mixed results. The basic idea of using ozone and hydroxyl radical in a two stage plasma chemical reactor to remove NO<sub>x</sub> from automotive exhaust proved to be correct. However we found the energy needed to operate the plasma chemical reactor is 30% of the engine's output, which is three times larger than that of the conventional catalytic converter. Our project is a partial success. If compactness is dropped as a requirement for our plasma-chemical reactor so that it is applicable to stationary rather than mobile power generators, then the reactor needs only 5% of the engine's power.. The energy inefficient component of the reactor, the part which makes our reactor compact, would be unnecessary. Thus our reactor has the potential for being a practical device to remove the NO<sub>x</sub> from the emissions of power plants.

This project has given LLNL visibility in plasma chemistry and toxic waste engineering. We reported our findings in two papers at the International Symposium on Plasma Chemistry, held in Minnesota from Aug. 23, 1995 to Aug 26, 1995. We found outside interest for our work, and received proposals for collaboration. However this interest did not materialize into funding, so our project is now dormant. Our project is also suffering for having an environmental flavor. In these times, environmental research and development projects are viewed as wasteful governmental spending which sows the seeds for new unnecessary regulations.

Let me summarize our successes and failures. We built and tested the OH generator. The production of OH by the breakdown of water cannot be maintained in a silent discharge tube, because OH rapidly destroys the glass lining of the tube (on the order of hours). As our experiment progressed, the production rate of the generator decreased, because of the degeneration of the glass lining. Even when the degeneration is accounted for, we found that the OH production rate of the silent discharge is about one third of what we expected. We failed to examine the effect of other combustion product gases (such as CO, H<sub>2</sub>O, ketones, etc.) on the oxidation of NO<sub>x</sub> by ozone and OH radicals, because we spent our time looking for the reason of the unexpected performance

of the OH generator. The high area to volume ratio of a silent discharge is unsuitable for the generation of OH, because OH destroys the glass walls of the discharge tube.

Let me describe our idea for the removal  $\text{NO}_x$  from air-like gas flows by optimizing its oxidation to nitric acid. The motivation for this work is to develop an efficient de- $\text{NO}_x$  process that can replace the catalytic converter of today's automobiles and recover greater engine performance.

The essence of the scheme is to optimize NO oxidation to  $\text{HNO}_3$  by relying on  $\text{O}_3$  injection, and then scrub the acid out through a granular NaOH filter, the final product being  $\text{NaNO}_3$ . The ozone is produced from air by an auxiliary discharge unit, and the filter would be replaced periodically. In theory this scheme could require less engine power than the enthalpy loss through the catalytic converter.

The intention of this scheme is to capture all the  $\text{NO}_x$  generated by engines operating with oxygen-rich fuel mixtures at high compression ratios for peak thermodynamic efficiency, and with minimal unburned hydrocarbon emission. Replacing the catalytic converter would also have the benefit of eliminating a future toxic waste to be reprocessed.

Pulsed plasma de- $\text{NO}_x$  schemes that employ discharges through the exhaust gas mixture are inefficient because they are not chemically specific, the electrical energy initiates a welter of competing chemical reactions. Also while the reduction of  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{O}_2$  would be ideal, this process requires more energy than its oxidation to nitric acid, its natural thermodynamic sink. The scheme presented here aims at chemical specificity by injecting radicals produced outside of the exhaust stream to both select the oxidation process and accelerate it.

Our experiments utilize a glass tube flow reactor with a 20 liter/minute flow mixed from the separate injections of compressed air and an admixture of 200 ppm of NO in nitrogen from a small pressurized bottle, for net proportions of 89%  $\text{N}_2$ , 11%  $\text{O}_2$ , 120 ppm NO. Ozone was produced in the airflow prior to its injection into the flow reactor by a coaxial barrier discharge. The discharge unit operates with an adjustable frequency repetitive pulsed power supply, and in this way initial ozone concentration could be selected.

NO quickly oxidizes to  $\text{NO}_2$  when the injected ozone concentration exceeds that of NO, and for  $\text{O}_3$  above 200 ppm no NO was detectable at the NO- $\text{NO}_2$  measurement

station 46 cm downstream of the mixing zone. When  $O_3$  increases beyond 100 ppm the concentration of  $NO_2$  always exceeds that of  $NO$ , and it peaks at about 80 ppm near the 200 to 300 ppm  $O_3$  level. With ozone between 800 to 1000 ppm the concentration of  $NO_2$  is between 50 to 60 ppm, and nitric acid is now seen at this same concentration. A chain of reactions involving  $O_3$  successively produce  $NO_2$ ,  $NO_3$ , and  $N_2O_5$  which then combines with ambient  $H_2O$  to form  $HNO_3$ .

The oxidation process could be accelerated even further by injecting  $OH$  into the  $NO_2$  flow to form  $HNO_3$  at a point sufficiently downstream of the ozone inlet that no  $NO$  remained. We have yet to produce a practical  $OH$  generator. Measurements of  $OH$  production in a pulsed corona discharge cell with an air-steam mixture indicate that the efficiency for producing this radical is at best eight times lower than for generating ozone.

We now turn to the  $OH$  generator. We will describe our measurement of  $OH$  concentration in a pulsed corona discharge through a steam-air mixture, and will also describe our model for the chemical kinetics of the  $OH$  generation. The motivation for the  $OH$  generator is to develop a the accelerator for the  $NO$  oxidation.

Time dependent measurements of the 3064 Å emission of  $OH$  indicate a production of nearly 4 ppm ( $\sim 10^{14} \text{ cm}^{-3}$ ) within a spark. This measurement was accomplished by a 1 ns resolution photomultiplier with a 100 Å filter centered at 3080 Å. The discharge occurs across a 1 cm coaxial gap between a central anode tube and an outer cylindrical cathode cased in glass and at ground potential. The water-air mixture is of equal proportions and at 1 atmosphere. Pulsed voltage of 38 kV and 60 ns risetime produces a 60 A, 20 ns FWHM spark.

The chemical kinetics model predicts the same  $OH$  production from the air-water mixture after 100 ns of  $10^{12} \text{ electrons/cm}^3$ . The electron density is set to zero during the subsequent interval of 100 ns in the model, and  $OH$  is seen to be produced by reactions of  $HO_2$  with oxygen and nitrogen atoms until these atoms have recombined into molecules, and the  $HO_2$  has been converted to  $H_2O_2$ .

The chemical kinetics model includes thirty four reactions involving the twelve species:  $H_2$ ,  $O_2$ ,  $NO$ ,  $N_2$ ,  $H_2O$ ,  $H$ ,  $O$ ,  $N$ ,  $OH$ ,  $HO_2$ ,  $H_2O_2$ , and  $O_3$ . Dissociation reactions predominate during the initial 100 ns discharge interval, and rate coefficients for dissociation are calculated from a Boltzmann model.

Hydrogen atoms disappear by combining with  $O_2$  to form  $HO_2$  during the initial 0.2 ms of electron-free evolution. During the subsequent evolution a cycle is observed in which OH reacts with atoms to form H and molecules, the hydrogen atoms are quickly converted to  $HO_2$ , and  $HO_2$  reacts with atoms to produce OH and molecules.

Oxygen atoms dominate this cycle for 20 ms until ozone formation has scavenged them, then only the slowly recombining nitrogen atoms are involved. Oxygen atoms favor a higher concentration of OH versus  $HO_2$  by their aggressive oxidation of  $HO_2$ , while nitrogen atoms favor  $HO_2$  over OH.

In the model  $HO_2$  decays by the slow process of  $H_2O_2$  formation, so it may be viewed as a stable fuel which produces OH when combined with atomic oxygen or nitrogen. OH itself is always short-lived, at one atmosphere under one microsecond. In summary, the high reactivity of OH limits its abundance.